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(54) **Process and composition for inhibiting iron and steel corrosion.**

(57) A composition and method for inhibiting the corrosion of iron and steel in the presence of aqueous acid at high temperatures comprising adding to the acid an effective corrosion-inhibiting amount of at least one iodide salt, at least compound selected from the group of formic acid compounds, formic acid derivatives, and formate esters, and an amine or a quaternary nitrogen compound, and/or an oxygen-containing compound such as a phenyl ketone, phenyl aldehyde, or an alkynol.

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PROCESS AND COMPOSITION FOR INHIBITING IRON AND STEEL CORROSION

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to a new and useful class of corrosion inhibitors, and a process of using them. The present invention provides novel compositions of matter which reduce the attack of aqueous acid solutions on ferrous metals at high temperatures, and a process of using them.

Technology Review

In the exploration and recovery of oil from underground fields, it is common to "acidize" both new and producing wells with aqueous solutions of strong acids. Various inhibitors for preventing the attack of acids on ferrous metals have been proposed. Of the many inhibitors especially designed to prevent acid attack on well casings, very few provide satisfactory protection at high temperatures. Arsenic and/or various arsenic compounds were used as high temperature corrosion inhibitors, despite their toxic effect. The toxic nature of arsenic and its compounds, and their adverse effect on catalysts used in petroleum refineries, have caused an extensive search for new corrosion inhibitors.

Formic acid, formic acid derivatives and formate esters are used as corrosion inhibitor aids or are components in high temperature HCl formulations. U.S. Patent 3,779,935 to McDougall discloses a composition containing formic acid or formate esters. Good corrosion protection to 200°C is demonstrated. U.S. Patent 4,028,268 to Sullivan et al. discloses a composition containing a formic acid derivative, such as formamide, mixed together with a nitrogen heterocyclic base, an acetylenic alcohol, and a surfactant. Using various combinations of the four components, good corrosion protection to 165°C is reported.

Potassium iodide has been used as a corrosion inhibitor aid in HCl at temperatures up to 150°C. Soviet literature lists mixtures of KI with organic nitrogen compounds (including hexamethylenetetraamine), alkynols and sodium sulfate. These formulations are reported to be effective up to 140°C. See Petroleum Abstracts, 59,682 (1965), 75,917 (1966), 78,725 (1966) and 99,560 (1968).

It would be desirable to have a corrosion inhibitor which is useful in a broader number of situations. For example, highly concentrated hydrochloric acid is often employed in oil well stimulation treatment, but its use can lead to severe corrosion problems, especially at high temperatures. Thus, it would be desirable to have a corrosion inhibitor composition which could inhibit the acid corrosion of ferrous metals even in the presence of concentrated hydrochloric acid at high temperatures, and which is compatible with a variety of additives, for example, surfactants.

SUMMARY OF THE INVENTION

The invention provides a composition and method for inhibiting the corrosion of iron and steel in the presence of aqueous acid at high temperatures, especially concentrated hydrochloric acid at temperatures above about 100°C. The composition and method comprises adding to an aqueous acid an effective corrosion-inhibiting amount of at least one iodide salt and at least one compound selected from the group of formic acid compounds, formic acid derivatives, and formate esters, together with at least one nitrogen compound or at least one oxygen-containing compound, as hereinafter described. The composition and method of the invention are surprisingly effective in inhibiting the corrosion of iron and steel over a broad range of aqueous acid concentration at high temperatures.

It is an object of the invention to provide an improved composition for inhibiting iron and steel corrosion caused by a corrosive aqueous fluid, comprising an aqueous acid, at least one nitrogen compound or at least one oxygen-containing compound, at least one iodide salt and at least one compound selected from the group of formic acid, formic acid derivatives, and formic esters.

It is another object of the invention to provide an improved method for inhibiting iron and steel corrosion caused by a corrosive aqueous acid fluid, comprising mixing a corrosion-inhibiting amount of a composition including at least one iodide salt and at least one compound selected from the group of formic acid compounds, formic acid derivatives, and formate esters, at least one nitrogen compound or at least one

oxygen-containing compound, together with corrosive aqueous acid.

It is an advantage of the invention that the improved composition is surprisingly effective in inhibiting the corrosion of iron and steel over a broad range of aqueous acid concentrations at high temperatures.

It is another advantage of the invention that the improved method for inhibiting corrosion is especially effective in highly concentrated aqueous acid solutions at high temperatures.

DETAILED DESCRIPTION OF THE INVENTION

The corrosion inhibitors of the present invention include at least one iodide salt and at least one compound selected from the group of formic acid compounds, formic acid derivatives, and formate esters. The compositions also usually include a nitrogen compound, preferably a quaternary alkyl or aryl nitrogen compound or an alkyl amine, and/or an oxygen-containing compound such as a phenyl ketone, phenyl aldehyde, or an alkynol.

Formic acid compounds useful in the practice of the present invention have the structural formula:
HCOOR
where R is hydrogen a phenyl group, an alkyl group having 1 to 6 carbon atoms, a cycloalkyl group having 5 or 6 carbon atoms, or an alkenyl and alkynyl group having 2 to 6 carbon atoms, which are unsubstituted or contain inert functional groups such as -OH, -COOH, -SH, -COH, =C=O and $-NH_2$ which do not affect corrosion inhibiting properties.

Formic acid derivatives useful in the practice of the present invention include formamides of the structure:

where R is hydrogen, a phenyl group, an alkyl group having 1 to 6 carbon atoms, a cycloalkyl group having 5 or 6 carbon aroms, or an alkenyl and alkynyl groups having 2 to 6 carbon atoms, which are unsubstituted or contain inert functional groups selected from -COH, OH, =C=O, -COOH, -SH, and $-NH_2$ which do not affect corrosion inhibiting properties. Specific examples of formamides useful in the practice include formamide, dimethylformamide, diethylformamide, and the like.

Formic acid esters useful in the practice of the present invention have the structural formula:

$$H\overset{\overset{O}{\|}}{C}-Z$$

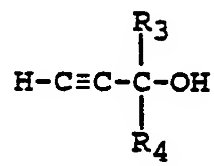
where Z is of an alkoxy group containing from about 1 to about 4 carbons atoms. Specific examples of formic acid esters useful in the practice of the present invention include methylformate, ethylformate, and butylformate.

Iodide salts useful in the practice in the present invention include alkali iodides, alkaline earth iodides, organic iodides, and hydrogen iodide. Potassium iodide and sodium iodide are normally preferred.

The nitrogen compounds useful in the process of the present invention include an aliphatic or aromatic quaternary compound, or an aliphatic or aromatic amine. Suitable aliphatic amines include saturated alkyl and unsaturated alkene amines, wherein each alkyl group may contain from 1 to about 20 carbon atoms and each alkene group may contain from 2 to about 20 carbon atoms. Preferably each aliphatic amine includes one long chain alkyl or alkene group containing from about 10 to about 20 carbon atoms, and two short chain alkyl groups containing from 1 to about 4 carbon atoms. Quaternary nitrogen compounds, also known as quaternary ammonium compounds, useful in the process of the present invention include saturated alkyl or unsaturated alkene quaternary compounds, aryl or alkylaryl quaternary compounds. Each alkyl group, including alkyl substituted aryl group, may contain from 1 to about 20 carbon atoms and each alkene group may contain from 2 about 20 carbon atoms. Suitable aromatic amines may be illustrated by pyridine; 2,6-dimethylpyridine (lutidine); hexahydropyridine (piperidine); quinoline; isoquinoline; alpha-methylquinoline (quinaldine); benzoquinoline; acridine; morpholine; and pyrimidine. Suitable quaternary compounds may be illustrated by C-alkyl pyridine-N-methyl chloride quaternary, C-alkyl pyridine-N-benzyl chloride quaternary, quinoline-N-benzyl chloride quaternary, isoquinoline-N-benzyl chloride quaternary, thioakyl pyridine quaternary, thioquinoline quaternary, benzoquinoline quaternary, thiobenzoquinoline quater-

nary, imidazole quaternary, pyrimidine quaternary, and carbazole quaternary. Any of these nitrogen compounds may be inertly substituted, that is substituted by groups which do not adversely affect the corrosion inhibiting properties of the corresponding unsubstituted composition. Tyical inert substituent include methyl, chloro, nitro, hydroxy, and methoxy. Unsubstituted or inertly substituted quinoliniums are normally preferred. For example naphthylmethylquinolinium chloride (NMQCl) may be used.

The composition of the present invention may optionally include an oxygen containing compound, such as an alkenylphenone. Examples of alkenylphenones include 2-benzyol-3--hydroxy-1-propene, 2-benzoyl-3-methoxy-1-propene, and 2-benzoyl-1,3-dimethoxypropane. The preparation of alkenylphenones is fully described in pending, commonly owned application Serial No. 06/765,890, incorporated herein by reference. Other oxygen containing compounds useful in the practice of the present invention include acetylenic alcohols such as ethyl octynol, propargyl alcohol, hexynol and other acetylenic alcohols having the structural formula:



where R_3 is selected from the group consisting of -H, and $-CH_3$, and R_4 is selected from the group consisting of hydrogen, alkyl groups having 1 to 18 carbon atoms, naphthalyl, phenyl and alkyl substituted phenyls having 1 to 10 carbon atoms in the alkyl substituent. Examples of such alcohols include methyl butynol, methyl pentyanol, hexynol, ethyl octynol, propargyl alcohol, benzyl butynol, naphthalyl butynol, and the like. Acetylentic alcohols having 3 to 10 carbon atoms are preferred.

The aqueous corrosive acid in the present invention is usually hydrochloric acid. However, other aqueous acids including organic or inorganic non-oxidizing acids may also be used. Examples of organic non-oxidizing acids include formic acid, acetic acid, and citric acid. Examples of non-oxidizing inorganic acids include sulfuric acid phosphoric acid, and hydrofluoric acid.

The composition of the present invention inhibits the attack of aqueous acid solutions on ferrous metals at ambient to high temperatures, especially concentrated aqueous acid at temperatures above about 100°C up to about 200°C. These compositions are also useful for treating oil and gas producing formations, and for cleaning hard surfaces such as utility boilers and heat exchangers. This inhibited acid solutions may be pumped into an oil or gas well for the purpose of stimulating the increased production of hydrocarbons. The dissolution of a carbonate or sandstone formation using an inhibited acid solution is an important technique for increasing the production of oil and gas. The compositions of the present invention allow this process to be conducted at higher temperatures, and for longer contact times then previously possible, since the corrosion of the steel tubing is inhibited. Furthermore, since lower concentrations of an iodide salt and formic acid component are possible, the risk of damaging the carbonate or sandstone formation is also reduced.

The compositions of the present invention are prepared by mixing at least one iodide salt, and at least one compound selected from the group consisting of formic acid compounds, formic acid derivatives, and formate esters into an aqueous acid. A nitrogen compound as described above and/or an oxygen containing compound as described above is also included. The concentration of a non-oxidizing inorganic or organic acid in the composition of the present invention may vary from about 1 to 30% by weight, based on the entire weight of the composition. The concentration of a nitrogen compound as described above in the composition of the present invention may vary from about 0% to about 3% by weight, based on the entire weight of the composition. The concentration of an iodide salt in the composition of the present invention may vary from about 0.1 to about 5% by weight, based on the entire weight of the composition. The concentration of at least one compound selected from the group of formic acid compounds, formic acid derivatives, and formate esters in the composition of the present invention may vary from about 0.5 to about 15% by weight, based on the entire weight of the composition. The concentration of an oxygen-containing compound in the composition of the present invention may vary from about 0% to about 3% by weight, based on the entire weight of the composition. The remainder of the aqueous composition consists essentially of water.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In order that those skilled in the art may better understand how the present invention may be practiced, the following Examples are given by way of illustration and not by way of limitation. All parts and percentages are by weight, compared to the weight of the entire composition, unless otherwise noted.

In Table 1, a composition containing a mixture of 2-benzoyl-3-methoxy-1-propene and 2-benzoyl-1,3-dimethoxypropane (PK), a quinolinium compound, namely naphthylmethylquinolium chloride (NMQCl), potassium iodide, and formic acid was tested. The NMQCl was prepared by reflexing equimolar amounts of quinoline and chloromethylnaphthylene in methanol at 70 to 75°C for six hours. This mixture was recrystallized from ethanol. The NMQCl is light tan and 90% pure by chloride titration.

Corrosion tests were run using an EG & G Chandler Engineering autoclave at a temperature of 177°C for four hours. The corrosion rate (CR) in (g/m²) is calculated:

$CR = \Delta g \times 0.039$

where Δg is the weight change of the coupon in grams. Table 1 shows 4 hour corrosion rates.

TABLE 1

CORROSION RATES AT 177°C FOR N80 STEEL

PK	NMQCl	KI	Formic	Rate (g/cm²)
		15% HCl		
0.5g	0.5g	2g	--	0.42
0.5	0.5	--	5g	0.12
0.5	0.5	0.5	1	0.019
		28% HCl		
1.5	1.5	--	10	0.083
1.5	1.5	2	--	0.12
1.5	1.5	2	10	0.036
1.5	1.5	--	5	0.12
0.5	1.5	8	--	0.098
0.5	1.5	4	4	0.04

The combination of potassium iodide and formic acid gives corrosion rates that are lower than the individual components. In the case of 15% HCl, when the combination of potassium and formic acid is used the concentrations of each component are much lower than when the components are used individually.

A mixture of potassium iodide, formic acid and 2% by weight of the Mannich reaction product of phenylethanone, formaldehyde, and ammonia was also tested at 149°C for 4 hous. The results are set forth in Table 2.

In addition the Mannich reaction product described above, other nitrogen-containing reaction products are also useful as nitrogen compounds in the process of the present invention. Suitable nitrogen-containing reaction products are described in U.S. Patents 3,077,454 and 3,634,270 and 4,493,775, each of which is incorporated herein by reference. For example, the reaction product of an amine, a ketone, and an aldehyde, is described in U.S. Patent 3,634,270. Suitable amines include, for example, normal, iso-and

tertiary alkyl amines having from 1 to 20 or more carbon atoms in the alkyl substituent, dialkylamines having 1 to about 20 carbon atoms in each alkyl substituent, and alkyl diamines having from 1 to about 20 carbon atoms in the alkyl portions thereof. Some of the ketones found to be affective are the aliphatic and aryl substituted aliphatic ketones and mixtures thereof such as, for example, acetophenone, propiophenone, and 1-and 2-acetonaphthone. Aldehydes having from 1 to 16 or more carbon atoms may be used, for example formaldehyde, hexanal, octanal, benzaldehyde, and the like.

The reaction product of cyclohexylamine, formaldehyde, and acetophenone is described in U.S. Patent 4,493,775.

TABLE 2

CORROSION RATES AT 149°C

N80 STEEL FOR 4 HOURS

15% HCl

% KI	% HCOOH	Rate (g/cm^2)
--	--	0.049
0.6	--	0.026
--	0.5	0.023
0.15	0.35	0.020

28% HCl

% KI	% HCOOH	Rate (g/cm^2)
--	1.0	0.055
--	2.0	0.045
1.0	--	1.534
2.0	--	0.289
0.3	0.7	0.056
0.6	1.4	0.042

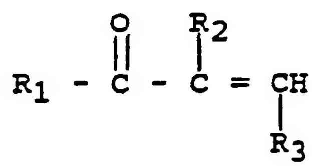
It is understood that various other modifications will be apparent to and can readily be made by those skilled in the art without departing from the scope and spirit of this invention. Accordingly, it is not intended that the scope of the claims appended hereto be limited to the description as set forth above, but rather that the claims be construed as encompassing all the features of patentable novelty which reside in the present invention, including all features which would be treated as equivalents thereof by those skilled in the art to which this invention pertains.

Claims

1. A corrosion inhibiting composition, comprising:
an effective corrosion inhibiting amount of at least an iodide salt, and
an effective corrosion inhibiting amount of at least one compound selected from the group consisting of formic acid compounds, formic acid derivatives, and formate esters.

2. A corrosion inhibiting composition, comprising:
at least one iodide salt,
at least one compound selected from the group consisting of formic acid compounds, formic acid derivatives, and formate esters, and
at least one compound selected from the group consisting of aliphatic and aromatic quaternary nitrogen compounds, and aliphatic or aromatic amines.

3. A corrosion inhibiting composition, comprising:
at least one iodide salt,
at least one compound selected from the group consisting of formic acid compounds, formic acid derivatives, and formate esters, and
at least one compound selected from the group consisting of alkenyl phenones of the formula:



wherein R_1 may be unsubstituted or inertly substituted aryl of 6 to 10 carbon atoms, and R_2 and R_3 may be the same or different and each may be hydrogen, halogen, or an unsubstituted or inertly substituted aliphatic of 1 to 12 carbon atoms, and acetylenic alcohols having 3 to 10 carbon atoms.

4. The corrosion inhibiting composition set forth in claim 2, including at least one oxygen-containing compound selected from the group consisting of alkenylphenones and acetylenic alcohols.

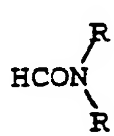
5. The corrosion inhibiting composition set forth in claim 1, wherein said iodide salt is sodium iodide or potassium iodide.

6. The corrosion inhibiting composition set forth in claim 1, including at least one iodide salt, and at least one formic acid compound.

7. The corrosion inhibiting composition set forth in claim 6, wherein said formic acid compound has the formula:
HCOOR
wherein R is hydrogen, a phenyl group, an alkyl group having one to six carbon atoms, a cycloalkyl group having five or six carbon atoms, or an alkenyl or alkynyl group having two to six carbon atoms, which are unsubstituted or inertly substituted.

8. The corrosion inhibiting composition set forth in claim 1, including at least one iodide salt, and at least one formic acid derivative.

9. The corrosion inhibiting composition set forth in claim 8, wherein said formic acid derivative is a formamide of the formula:



wherein R is hydrogen, a phenyl group, an alkyl group of one to six carbon atoms, a cycloalkyl group having five or six carbon atoms, or an alkenyl or alkynyl group having two to six carbon atoms, which are unsubstituted or inertly substituted.

10. The corrosion inhibiting composition set forth in claim 1, including at least one iodide salt, and at least one formic acid ester.

11. The corrosion inhibiting composition set forth in claim 10, wherein said formic acid ester is an ester of the formula:

$$H\overset{\overset{O}{\|}}{C}\text{-}Z$$

wherein Z is an alkoxy group of one to four carbon atoms.

12. The corrosion inhibiting composition set forth in claim 6, including at least one alkyl, alkenyl, aryl or alkylaryl quaternary nitrogen compound, said alkyl or alkyl substituent containing one to 20 carbon atoms and said alkenyl containing 2 to 20 carbon atoms.

13. The corrosion inhibiting composition set forth in claim 12, wherein said quaternary nitrogen compound is a quinolinium.

14. The corrosion inhibiting composition set forth in claim 6, including at least one alkyl or alkenyl amine, said alkyl or alkenyl including one alkyl or alkene group containing from 10 to 20 carbon atoms and two alkyl groups containing from 1 to 4 carbon atoms.

15. The corrosion inhibiting composition set forth in claim 8, including at least one aryl, alkenyl, aryl or alkylaryl quaternary nitrogen compound, said alkyl or alkyl-substituent containing one to six carbon atoms and said alkenyl containing 2 to 20 carbon atoms.

16. The corrosion inhibiting composition set forth in claim 15, wherein said quaternary nitrogen compound is a quinolinium.

17. The corrosion inhibiting composition set forth in claim 8, including at least one alkyl or alkenyl amine, said alkyl or alkenyl including one alkyl or alkene group containing from 10 to 20 carbon atoms and two alkyl groups containing from 1 to 4 carbon atoms.

18. The corrosion inhibiting composition set forth in claim 10, including at least one alkyl, alkenyl, aryl or alkylaryl quaternary nitrogen compound, said alkyl or alkyl-substituent containing one to six carbon atoms and said alkenyl containing 2 to 20 carbon atoms.

19. The corrosion inhibiting composition set forth in claim 18, wherein said quaternary nitrogen compound is a quinolinium.

20. The corrosion inhibiting composition set forth in claim 10, including at least one alkyl or alkenyl amine, said alkyl or alkenyl including one alkyl or alkene group containing from 10 to 20 carbon atoms and two alkyl groups containing from 1 to 4 carbon atoms.

European Patent Office

EUROPEAN SEARCH REPORT

Application number

EP 88200047.4

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl 4)
A	AT - B - 149 199 (R. BÜRSTEN-BINDER) * Claim 2 * --	1,5-7	C 23 F 11/12 C 23 F 11/14 C 23 F 11/18
A	DE - A1 - 2 638 305 (J.W. AIDLIN) * Claim 2 * --	1,5,6	
A	US - A - 2 907 699 (A.F. MILLIDGE et al.) * Examples 1-5 * --	1,5-7	
A	DE - B - 1 185 036 (CONTINENTAL OIL COMPANY) * Column 2; claims * --	2	
A	EP - A2 - 0 209 978 (SEALED AIR CORPORATION) * Claims * --	2	TECHNICAL FIELDS SEARCHED (Int. Cl.4) C 23 F
A	US - A - 4 562 042 (F. MORAN) * Examples; claims * --	2	
P,A	EP - A1 - 0 212 752 (DOWELL SCHLUM-BERGER INCORPORATED) * Abstract; claims * ----	3,4	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
VIENNA	22-03-1988	SLAMA

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
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E : earlier patent document, but published on, or after the filing date
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